Renormalized behavior and proximity of BaCo$_2$As$_2$ to a magnetic quantum critical point

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We report synthesis and single-crystal measurements of magnetic, transport, and thermal properties of single crystalline BaCo$_2$As$_2$, as well as first-principles calculations of the electronic structure and magnetic behavior. These results show that BaCo$_2$As$_2$ is a highly renormalized paramagnet in proximity to a quantum critical point, presumably of ferromagnetic character and that BaFeNi$_2$As$_2$ behaves similarly. These results are discussed in relation to the properties of Ba(Fe,Co)$_2$As$_2$ and Ba(Fe,Ni)$_2$As$_2$, which are superconducting for low Co and Ni concentrations.

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The discovery of high-temperature superconductivity in oxynitride phases, prototype LaFeAs(O,F) by Kamihara and et al.\textsuperscript{1} has led to strong interest in establishing the physical properties of these materials and the mechanism of superconductivity. Since the discovery, superconductivity has been found in a rather wide variety of compounds with Fe$^{2+}$ square planar sheets. These include the oxynitrides, doped ThCr$_2$Si$_2$ structure compounds of, e.g., BaFe$_2$As$_2$,\textsuperscript{2} LiFeAs,\textsuperscript{3} and FeSe\textsuperscript{4}. Remarkably, superconductivity can be produced in BaFe$_2$As$_2$ by alloying Fe with the other ferromagnetic 3$d$ elements, Co or Ni.\textsuperscript{5,6} As is also found in the oxynitrides.\textsuperscript{7} Interestingly, both the Ni-based oxynitride and BaNi$_2$As$_2$ are superconductors,$\textsuperscript{8-10}$ although the critical temperatures are much lower than in the Fe-based compounds and the pairing mechanism may be different\textsuperscript{11,12} Also, LaCoAsO and LaCoPO are itinerant ferromagnets.\textsuperscript{7,13}

The single crystals of BaCo$_2$As$_2$ were grown out of CoAs flux. The typical crystal sizes were $\sim 5 \times 3 \times 0.2$ mm$^3$. High purity elements ($>99.9\%$, from Alfa Aesar) were used in the preparation of the crystals. First, CoAs binary was prepared by placing mixtures of arsenic pieces, and cobalt powder in a preparation of the crystals. First, CoAs binary was prepared by placing mixtures of arsenic pieces, and cobalt powder in a silica tube. These were reacted slowly by heating to 300 $^\circ$C (dwell 10 h), to 600 $^\circ$C (dwell 10 h), then to 900 $^\circ$C (dwell 10 h). Then, a ratio of Ba:CoAs=1:5 was heated in an alumina crucible for 15 h at 1180 $^\circ$C under a partial atmosphere of argon. This reaction was cooled at the rate of 2 $^\circ$C/h, followed by decanting of CoAs flux at 1090 $^\circ$C. The crystals were well-formed plates with the [001] direction perpendicular to the plane. Electron probe microanalysis of a cleaved surface of the single crystal was performed on a JEOL JSM-840 scanning electron microscope using an accelerating voltage of 15 kV and a current of 20 nA with an EDAX brand energy-dispersive x-ray spectroscopy (EDS) device. EDS analyzes indicated Ba:Co:As ratio of 1:2:2. The structural identification was made via powder x-ray diffraction using a PANalytical X’pert Pro MPD with an X’celerator position sensitive detector (Cu $\text{K}a$ radiation). The cell parameters were refined from full pattern LaBail fits using the program FullProf.\textsuperscript{14} The lattice parameters of BaCo$_2$As$_2$ are $a=3.9537(1)$ Å, and $c=12.6524(6)$ Å, in the ThCr$_2$Si$_2$ structure ($I4/mmm$, $Z=2$) in close agreement with the report of Ref. 15.

Dc magnetization was measured as a function of temperature and field using a Quantum Design magnetic property measurement system (PPMS). Figure 1 shows the susceptibility in 1 kOe applied field along $c$- and $ab$-crystallographic directions. The susceptibility is weakly anisotropic and decreases with increasing temperature. At 1.8 K, $\chi_c=5.4 \times 10^{-3}$ cm$^3$ mol$^{-1}$ and $\chi_{ab}=3.8 \times 10^{-3}$ cm$^3$ mol$^{-1}$. As seen in the inset of Fig. 1, the field dependent magnetization is linear at 1.8 K.

Temperature dependent electrical resistivity measurements were performed on a Quantum Design PPMS, measured in both the $ab$ plane ($\rho_{ab}$) and $c$ direction ($\rho_c$). As shown in Fig. 2, both $\rho_{ab}$ and $\rho_c$ decrease with decreasing temperature, revealing metallic behavior. However, the resistivity is much more anisotropic than the magnetic susceptibility. At room temperature $\rho_{ab}$=0.07 m$\Omega$ cm and $\rho_c$=2.7 m$\Omega$ cm, resulting in $\rho_c/\rho_{ab} \approx 39$. In analyzing the low-temperature data, we found that both $\rho_{ab}$ and $\rho_c$ exhibit quadratic temperature dependencies in a wide temperature range. Shown in the inset of Fig. 2 is the plot of $\rho_{ab}(T)$ and $\rho_c(T)$ between 1.8 and 71 K. Note that $\rho_{ab}$ and $\rho_c$ vary approximately linearly with $T^2$ below $\sim 60$ K. By fitting the resistivity data between 1.8 and 60 K using $\rho_{ab,c}=\rho_{ab,c}(0 \text{ K}) + AT^2$, we obtain the residual resistivity $\rho_{ab,c}(0 \text{ K})=5.75 \mu\Omega$ cm, $\rho_c(0 \text{ K})=0.22 \mu\Omega$ cm, and constant $A_{ab,c}=2.22 \times 10^{-3} \mu\Omega$ cm/K$^2$, $A_c=9.65 \times 10^{-2} \mu\Omega$ cm/K$^2$. These give the residual-resistivity-ratio ($\rho_{300 \text{ K}}/\rho_{0 \text{ K}}$) $\approx 12$.

![FIG. 1. Magnetic measurements for BaCo$_2$As$_2$ along the two crystallographic directions. The figure is the temperature dependence of the zero-field cooled magnetization in 1 kOe; inset is the field dependence of the magnetization at 1.8 K.](image-url)
hybridization with ligands, which is not evident in the electronic structure, or substantial renormalization due to e.g., spin fluctuations. Assuming that \( \chi_c = 5.4 \times 10^{-3} \text{ mol}^{-1} \) and \( \chi_{ab} = 3.8 \times 10^{-5} \text{ mol}^{-1} \) at 1.8 K are spin susceptibilities (i.e., assuming that the diamagnetic and van Vleck contributions are small), we may estimate the Wilson ratio \( R_W = \pi^2 k_B \chi_{spin}/(3\mu_B^2 \gamma) \). This gives \( R_W \approx 7 \) from \( \chi_{ab} \) and \( \approx 10 \) from \( \chi_c \). These values well exceed unity for a free-electron system and are indicative of enhanced magnetic behavior. There are several possible reasons for high \( R_W \): one is that actual low-temperature spin susceptibility is much smaller than the total susceptibility, e.g., due to a strong orbital contribution. Another source of enhancement can be strong Coulomb correlations, which often result in Wilson ratios intermediate between 1.5 and 2.0. However, the large value that we find, which is of order of magnitude higher, is best explained as indicating that the system is close to ferromagnetism. Combined with the high \( R_W \), we find a normal Kadowaki-Woods ratio \( \Lambda/\gamma^2 \). In particular, for BaCo\(_2\)As\(_2\) in-plane transport we obtain \( \Lambda_{ab}/\gamma^2 = 0.1 \times 10^{-7} \mu\Omega \text{ cm/(mol K)}^2 \). This is comparable to the value for the nearly two-dimensional Fermi liquid, Sr\(_2\)RuO\(_4\), smaller than the typical value of \( 10^{-5} \mu\Omega \text{ cm/(mol k)}^2 \) for heavy Fermions, and significantly smaller than the values found in correlated oxides with frustration or other very strong scattering such as LiV\(_2\)O\(_4\) or La\(_{1.7}\)Sr\(_{0.3}\)CuO\(_4\).\(^{10}\)

Electronic structure calculations were performed using the general potential linearized augmented plane-wave (LAPW) method with local orbitals.\(^{17,18}\) Similar to those reported previously for BaFe\(_2\)As\(_2\).\(^{19}\) The calculations used LAPW sphere radii of 2.2\(a_0\), 2.1\(a_0\), and 2.1\(a_0\) for Ba, Co, and As, respectively, and were done within the local-density approximation (LDA) with reported lattice parameters of \( a = 3.958 \AA \), and \( c = 12.67 \AA \).\(^{15}\) The As internal coordinate \( z_{\text{As}} \) was obtained by energy minimization as \( z_{\text{As}} = 0.3458 \). This value is somewhat smaller than the value that we obtained by x-ray refinement of \( z_{\text{As}} = 0.38 \). The discrepancy between the calculated and experimental values of the As height is in the same direction as in the superconducting Fe-based phases, but is less severe. For example, the calculated value\(^{19}\) for tetragonal BaFe\(_2\)As\(_2\) obtained in the same way is \( z_{\text{As}} = 0.342 \) as compared to the experimental value of \( z_{\text{As}} = 0.3545 \) (Ref. 20), yielding a twice larger discrepancy. The discrepancy is also roughly twice larger for the Fe-chalcogenide superconductors.\(^{21}\) In the Fe-based materials this discrepancy is thought to be associated with magnetism, and in particular strong spin fluctuations.\(^{22}\) The significant, though smaller, deviation in the present compound may therefore also be an indication of effects of spin fluctuations.

The calculated electronic density of states and Fermi surface for the calculated LDA \( z_{\text{As}} \) are shown in Figs. 4 and 5. The DOS is rather similar to that of the Fe compounds with the exception of the position of the Fermi energy. In particular, it shows only modest covalency between Co and As, and has a pseudogap at an electron count of six \( d \) electrons per Co. The extra \( d \) electron in Co\(^{2+}\) relative to Fe\(^{2+}\) shifts \( E_F \) upwards into a region of high DOS. The Fermi surface is large and multisheeted, as shown in Fig. 5. The calculated Fermi surface has both two and three dimensional sheets, and in particular is more three dimensional than might be
expected based on the anisotropy of the measured resistivity. Reconciling the Fermi surface with the transport data would require scattering that depends on the particular Fermi surface sheet, as may occur, for example, from spin fluctuations with a large anisotropy or due to strong band dependence of the electron-phonon scattering. The main As contributions to the DOS are between −6 and −3 eV relative to $E_F$, corresponding to stable As$^{3-}$ and Co$^{2+}$. The value at the Fermi energy is $N(E_F)/N_0 = 8.5$ eV$^{-1}$ on a per f.u. two Co atoms both spins basis. Comparing with the measured specific heat implies a mass renormalization of 2, similar to the Fe-based superconductors. As shown in the inset of Fig. 3, our measured value for BaNi$_2$As$_2$ is $Y = 15$ mJ/(mol K$^2$), as compared with a bare value from $N(E_F)$ of 8.9 mJ/(mol K$^2$). This yields an enhancement factor of $(1+\lambda) = 1.7$, consistent with the value of the electron-phonon $\lambda = 0.76$ obtained from first-principles calculations for that compound.$^{12}$

The physics, however, appears different in BaCo$_2$As$_2$ from that in BaNi$_2$As$_2$. First of all, the susceptibility implied by the magnetization measurements is enhanced over the Pauli susceptibility from the LDA density of states, $\chi_0 = 2.75 \times 10^{-4}$ emu/mol by a factor of $\sim 15$ (depending on direction) yielding a high Wilson ratio with implied nearness to ferromagnetism. Furthermore, the nonrenormalized LDA $N(E_F)$ is already large enough to lead to a mean-field Stoner instability toward ferromagnetism. In fact, contrary to experiment we find a stable ferromagnetic ground state in the LDA, with spin moment 0.94 $\mu_B$/f.u. and energy 32 meV/f.u. lower than the non-spin-polarized solution. The total energy as a function of constrained moment is shown in Fig. 6. We also searched for an antiferromagnetic solution with a checkerboard in-plane arrangement where all nearest-neighbor Co bonds are antiferromagnetic. However, we did not find a stable antiferromagnetic state of this type. This indicates that the stability of Co moments depends on the particular magnetic order and therefore that the magnetism is itinerant. Thus at the LDA level, BaCo$_2$As$_2$ is a weak itinerant magnet, apparently ferromagnetic in-plane, though the out-of-plane interaction may be ferromagnetic or antiferromagnetic.

While the mechanism for superconductivity of the layered Fe compounds remains to be established, there is accumulating evidence of a relationship between superconductivity and magnetism. For example, the phase diagrams show an interplay between of an itinerant spin-density wave (SDW) with superconductivity,$^{20,23}$ and density-functional calculations show a proximity to magnetism, with evidence for strong spin fluctuations.$^{22,24-26}$ Other evidence for strong magnetic effects comes from the unusual temperature dependence of the susceptibility, $\chi(T)$, which for some compounds is increasing with $T$ up to high $T$,$^{27,28}$ and unusually large dis-
crepancies between calculated and measured pnictogen crystallographic positions. An important signature of the beyond mean-field spin-fluctuation effects in the Fe-based superconductors is the fact that standard density-functional calculations give much more robust magnetic moments than experiment.

Comparing our experimental and calculated results for BaCo$_2$As$_2$, we find a related situation. In particular, we do not find clear evidence in transport or magnetization data for a magnetic ordering (there is a change in behavior of the magnetization at ~60 K but the susceptibility continues increasing below this temperature, and we do not find any hysteresis). The implication is that the LDA yields a more magnetic state than experiment. This generally occurs in materials near a magnetic quantum critical point, where ordering is suppressed by quantum fluctuations in the order parameter (i.e., spin fluctuations). Examples of this behavior include the weak itinerant ferromagnets ZrZn$_4$, Ni$_3$Al, and the highly renormalized paramagnets Ni$_3$Ga and Sr$_2$RuO$_4$, although the renormalizations in those materials are apparently stronger than in our measurements for BaCo$_2$As$_2$.

Further information comes from our single-crystal measurements for BaFeNiAs$_2$, which was prepared in a similar way to BaCo$_2$As$_2$, using a near equal atomic mixture of Fe and Ni to obtain approximately the same average $d$ electron count as BaCo$_2$As$_2$. The single crystals of BaFeNiAs$_2$ were grown using a procedure similar to that described above for BaCo$_2$As$_2$. The lattice parameters of BaFeNiAs$_2$ are $a = 4.0002(1)$ Å, and $c = 12.6767(3)$ Å, in the ThCr$_2$Si$_2$ structure. The measured specific heat $\gamma$ (Fig. 3) is remarkably similar to those for BaCo$_2$As$_2$. Therefore, at least for these properties, which include the renormalization, the material behaves as a virtual crystal, meaning that the alloy of Fe and Ni behaves in many respects as if it were a true pure compound of the element with the average atomic number (i.e., Co for an equal mixture). In this way, scattering is not strong enough to alter the basic electronic structure, a fact that may be of importance in understanding why superconductivity in the BaFe$_2$As$_2$ is robust against the disorder introduced by alloying with Co or Ni.

Our results show no evidence of superconductivity in BaCo$_2$As$_2$. This is as might be anticipated. While the electronic structure is formed in a similar fashion to those of BaFe$_2$As$_2$ and superconducting Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$, the electron count is higher leading to a very different electronic structure at $E_F$. In particular, the topology of the Fermi surface is very different. Furthermore, even though both the Fe and Co compounds are near itinerant magnetism, the nature of the magnetism is very different. The Fe compounds are near a SDW associated with Fermi-surface nesting, while BaCo$_2$As$_2$ is near ferromagnetism. Unlike spin fluctuations associated with an SDW, which are pairing for, e.g., singlet $s_\pm$ superconductivity, ferromagnetic spin fluctuations are strongly pair breaking for any singlet superconductivity, including electron-phonon superconductivity. Considering the present results for the electronic structure, one possibility for producing high-temperature superconductivity based on cobalt would be to lower the electron count to move the material away from ferromagnetism and to produce a Fermi surface similar to the Fe-based materials. In this regard, Co$^{3+}$ is a chemically stable valence for Co (as in e.g., LaCoO$_3$ and LiCoO$_2$). Furthermore, KCo$_2$As$_2$ is a known ThCr$_2$Si$_2$ structure compound, which might conceivably be the basis of a Co superconductor if the electron count could be further lowered, e.g., through K vacancies or alloying of As with a group IV element.

To summarize, we find from comparison of experimental data on single crystals and LDA calculations that BaCo$_2$As$_2$ is a substantially renormalized metal near a magnetic quantum critical point, probably of ferromagnetic character. It will be of interest to tune the proximity to the critical point. One interesting possibility would be to alloy on the Ba site with a magnetic element, e.g., Eu, which may favor formation of a magnetically ordered state.

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